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微波-活性炭组合技术在难生化废水降解中的应用研究

The research of the refractory wastewater with the microwave combined with actived carbon processes

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摘 要

难生化降解废水通常是指废水中含有许多难以被微生物分解彻底的有机污染物，主要来源于机械加工、印染、生活垃圾等行业，因其种类多、排放量大、COD含量高，成分复杂，含有大量难生化降解有机物，会对周围环境和地下水造成严重污染。难生化废水还因其水质变化大、微生物营养元素比例失调、可生化性差等特点，使得目前普遍使用的处理技术难以达到理想的处理效果。本研究针对这一难点和热点问题，试图寻找一种新技术以能更好地解决这个问题。

本文采用微波-活性炭组合的新工艺，在微波辐照条件下，以活性炭为催化剂，以石英玻璃为介质管动态连续地处理不同种类的高浓度难生化有机废水来考察这种新工艺的实用可行性。主要开展了以下几方面的工作：

（1）运用微波-活性炭组合技术对含油乳化液进行破乳研究。乳化液初始含油量为62.35 mg/L，初始COD高达198.66 g/L，在微波功率1000 W，水流量为0.5 m^3/h，搅拌速度为70 r/min，处理60 min，静置30 min条件下催化破乳，实验结果表明：随着辐射时间的增加，含油乳化液中含油量逐渐减少，处理时间为40 min时，油的除去率可达到89.2%，COD去除率可达到69.5%。其破乳机理本文认为是微波破坏油-水界面的双电层，降低Zeta电位，破坏原先稳定的乳化液体系，加速了油水分离进程。

（2）以脱色率为指标考察微波-活性炭组合技术对甲基红染料溶液的脱色效果。实验中考察了甲基红浓度、活性炭用量、微波辐射时间和微波辐射功率对甲基红的去除效果的影响。结果表明微波-活性炭组合工艺对甲基红的处理效果明显优于微波直接处理处理的效果。当染料初始浓度为10 mg/L，微波功率1000 W，水流量为0.5 m^3/h，加入20 g活性炭和等量的铁屑，处理40 min时，发现脱色效果较好。紫外光谱分析结果推测甲基红经微波催化氧化处理后，分子结构中的偶氮键发生断裂，破坏了偶氮-苯环共轭发色体系，达到了脱色的目的。其脱色的主要机理本文推测是由于废水中发生铁屑/炭内电解反应，生成的新生态的氢和裸露的铁原子改变了发色团结构，从而实现染料脱色的目的。

（3）以BOD/COD为指标，考察微波-活性炭组合工艺对城市生活垃圾渗滤液的处理效果。实验结果表明在微波功率1000 W，辐射时间40 min，20 g吸附饱和

的活性炭等条件下，COD 含量由原来的 37.66 g/L 降到 29.90 g/L，BOD/COD 由原来的 0.5 提高到 0.9，提高了垃圾渗滤液的可生化性，并且在实验过程中发现 BOD 含量不断持续上升，由原来的 18.90 g/L 上升到 28.80 g/L，这种现象在国内相关文献报道较为少见，至于其具体机理和变化规律尚未看到相关报道。本文从机理分析，认为在微波处理难生化废水过程中，存在着“热效应”和“非热效应”。微波通过改变难生化有机物中的分子排列等焓或熵效应来降低反应活化能，从而改变反应的动力学，促进反应进程。

本文研究表明微波-活性炭组合技术是处理难生化废水的一种新型水处理技术。该工艺主要有两个特点：（1）废水运行管理费用低，转化 1 kg BOD 的实际费用成本大约是 0.39 元，经济成本低，故常可作为预处理技术；（2）处理效率高，在一定条件下，可把 BOD/COD 的比值从 0.5 提高到 0.9，可大幅度提高废水的可生化性。该工艺作为预处理技术，由于可降低其经济成本和提高可生化性，因此增强了实际应用可行性。

另外本工艺除了以上优点外，还有占地面积小、施工期短、水质水量波动适应性强和不受气候条件影响等优点。该工艺在难生化废水处理领域有很大的发展前景，但由于本工艺现处于小试阶段，其工业化应用影响因素及处理效果还有待中试实验进一步考察和研究。

通过电镜扫描，发现微波辐射后的活性炭表面有明显的灼烧痕迹，为了考察活性炭的再生性能，本实验还做了微波辐射前后的活性炭的亚甲基蓝吸附对比实验，发现微波辐射后的活性炭吸附性能比未经过微波辐射的活性炭吸附性能提高了 15%。因此本文推测活性炭在微波场中发生“微域爆炸”导致其表面及内部孔隙结构发生变化，从而实现再生，其吸附性能也得到了有效改善，这个也是难生化有机物能被活性炭持续吸附及去除的一个重要原因。

目前微波降解难生化废水的研究已显示出诸多优点，然而微波化学技术距离产业化还存在两个亟待解决的问题—经济成本问题和成熟的设备问题。而本项目的实施不仅可降低经济成本，其运用的成熟设备也将解决难降解废水处理的难题，因此本项目对于微波技术应用于实际表现了更大的可行性和先进性。

关键词：微波-活性炭；水处理技术；催化氧化；破乳；脱色；可生化性

Abstract

Biorefractory wastewater often means that wastewater contains many organic pollutants which is difficult to be completely decomposed by microbe and which mainly comes from industries such as machining, dyeing and finishing, domestic garbage and so on. Biorefractory wastewater can pollute seriously its surroundings and groundwater because of its wide variety of types, great amount of discharge, high COD content, complex element and a great quantity of biorefractory organic compounds. According to the characteristic of biorefractory wastewater which has water quality fluctuation, microbial nutrient imbalance, low biochemical degradation and so on, it is hard to be dealt with effectively by the current commonly used technology. The research aims at this difficult as well as hot issue and tries to find out a new technology to solve this problem.

This paper adopts the mew method of microwave heating with active carbon, under microwave irradiation, using activated carbon as catalyst, quartz glass as medium pipe, continuously dealing with different types of high concentration and refractory organic wastewater to investigate the possibility of its practical application. Research work is made on the following aspects:

(1) Research on the demulsification of oily emulsified liquid with the help of microwave-activated carbon combination technique. The initial content of oil in emulsified liquid is 62.35 mg/L, and the initial concentration of COD reaches up to 198.66 g/L, when microwave power is 1000 W, the rate of water flow is 0.5 m3/h, stirring speed is 70 r/min, the handling time lasts for 60 min, thus it is possible to catalytically break the emulsion under the condition of 30 min standing. The results of experiment show that: the content of oil in emulsified liquid gradually decreases with the increase of radiation time, when the handling time is 40 hours, the removal rate of oil can reach up to 89.2%, and the strainaway rate of COD is 69.5%. In this paper, it is considered that the mechanism of demulsification is that microwave breaks the double electrode layer of oil-water interface, cuts down Zeta electric potential, and destroys the original system of emulsified liquid which is stable enough, so as to accelerate the speed

of oil-water separation process.

(2) Observe and study the discoloration effect of microwave-activated carbon combination technique on methyl red dye solution by taking the discoloring ratio as the index. In the experiment, the impact of methyl red concentration, dosage of activated carbon, action time and power of microwave radiation on the removal of methyl red has been investigated. And the results indicate that the treatment effect of microwave-activated carbon combination technique shows a better performance than that of direct treatment by microwave. When the initial concentration of dye solution is 10 mg/L, microwave power is 1000 W, and the rate of water flow is 0.5m3/h, 20g activated carbon and 20g scrap iron are added, after treatment for 40min, the effect of discoloration is good. Based on the ultraviolet spectrum analysis results, it is deduced that after methyl red has been catalytically oxidized by microwave, azo bond in its molecular structure is broken, which can destroy azo-benzene ring conjugated chromophoric system, to achieve the purpose of discoloration. In this paper, it is deduced that the main mechanism of discoloration is that scrap iron/carbon internal electrolytic reaction happens in the waste water, thus new hydrogen and bare Fe have changed the structure of chromophore, so as to realize the goal of dye discoloration.

(3) Use BOD/COD ratio as an indicator to study the affects of microwave - GAC process on the results of city life landfill leachate treatment. Results show that under the condition of 1000W of microwave power, 20 g of adsorption saturated activated carbon and 40min of irradiation time, the content of COD dropped from 37.66 g/L down to 29.90 g/L, and BOD/COD ratio increased from 0.5 to 0.9, which improved the biodegradability of landfill leachate. What's more, during the experiments it was found that the level of BOD kept rising, from 18.90 g/L up to 28.80 g/L. This phenomenon is so rarely reported in the related articles of our country that its specific mechanism and law of variation have not been seen in the relevant reports. Basic on the analysis of mechanism, this paper believes that there exist "heat effect" and "non-thermal effect" during the treatment for difficult biochemistry degradation wastewater by microwave. Microwave changes the molecular arrangement of the difficult biochemistry degradation organics. This process is called enthalpy or entropy effect which can reduce

the reaction activation energy. Thus it can change the kinetics of reactions to promote reaction process.

This paper shows that the microwave-activated carbon combination technology is a new type of treatment for difficult biochemistry degradation wastewater. This technology has two main characteristics. The first one is its low cost for operation and management. The actual cost is about 0.39 yuan to convert 1 kg BOD. Because of its low economic cost, it can be used as a pretreatment technology. The second is its high efficiency. In certain conditions, it can increase the BOD/COD ratio from 0.5 to 0.9, which can greatly improve the biodegradability of the wastewater. Low economic cost and high efficiency enhance its feasibility of practical application as a pretreatment technology.

Moreover, it has other advantages, such as less premise, short construction period, strong adaptability to the fluctuations of water quality and quantity and less impact from climatic conditions. This technology has a great prospect in the area of treatment for difficult biochemistry degradation wastewater. Since it is still in the test period, its influencing factors of industrial applications and treatment results need to be investigated and studies further.

Scanning by electron microscope, it found there existed obvious burning traces on the surface of activated carbon after radiation of and found that microwave in this experiment. In order to examine the regeneration ability of activated carbon, this study also made comparison experiments of the Methylene Blue capacity between before and after the microwave radiation. It was found that the activated carbon after the microwave radiation had 15% higher the carbon adsorption of performance than that without. Thus, this paper infers that activated carbon has micro domain explosion in the microwave radiation, leading to the changes of inner and outside pore configuration. In this process, the activated carbon comes to regeneration, and its adsorption ability improves effectively at the same time. This is an important reason for that the difficult biochemistry degradation organics can be continuously absorbed and removed by activated carbon. Recently, it shows many advantages to use microwave to degrade

difficult biochemistry degradation wastewater. However, two problems need to be solved before the industrialization of the technology of microwave chemistry-the economic costs and sophisticated equipment. The implementation of this project can reduce the economic costs, and the use of sophisticated equipment can also solve the difficult problem to deal with hard-degradation waste water. In a word, this project shows greater feasibility and advancement for the actual practice of microwave technology.

Keyword: Microwave-activated carbon; Technology of water treatment; Catalytic oxidation; Demulsification; Decoloration; Biodegradability

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